

Progress Report for year 1 covering the period  
June 1, 2000 – May 30, 2001

## **Horizontal Ampoule Growth and Characterization of Mercuric Iodide at Controlled Gas Pressures for X-Ray and Gamma Ray Spectrometers**

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### **Introduction**

The following described DOE sponsored Nuclear Engineering Educational Research (NEER) program addresses a new method for producing high quality mercuric iodide ( $\text{HgI}_2$ ) crystals for radiation spectrometers.  $\text{HgI}_2$  is a semiconductor material with a relatively wide band gap of 2.13 eV that serves to significantly reduce thermal leakage current noise at room temperature. Additionally, the elements comprising the material have high atomic numbers, being 53 for iodine and 80 for mercury, important physical attributes that significantly increase the gamma-ray absorption probability over semiconductor materials that have been traditionally used. For instance, a 2 mm thick piece of  $\text{HgI}_2$  will undergo photoelectric absorption for the same fraction of 100 keV gamma rays as a 2 cm thick piece of Ge.

Yet,  $\text{HgI}_2$  comes with its own unique set of difficulties. Unlike common semiconductors used in the VLSI industry,  $\text{HgI}_2$  is non-cubic, forming in a tetragonal crystal structure (noted as the  $\alpha$ -phase) at temperatures below 130°C. At temperatures above 130°C, the crystal undergoes a phase change and forms in an orthorhombic crystal structure, noted as the  $\beta$ -phase, and if cooled below 130°C destructively turns to the  $\alpha$ -phase. Hence, the crystal must be grown such that the material does not crystallize at temperatures above 130°C along with the additional constraint that detectors fabricated from the material must not be stored or operated in environments that may allow for the critical temperature of 130°C to be reached.

As with any semiconductor used for gamma radiation spectroscopy, reduction of impurities is of major importance. The presence of impurities cause the appearance of

trapping sites, hinder the transport properties of charge carriers, and cause distortions in the electric field distribution. Thus the production of high-quality  $\text{HgI}_2$  spectrometers requires careful handling of the material during pre-growth, growth, and post-growth stages, since impurities may be introduced in some or all of these stages.

A method by S. Faile in 1981 has been widely used to produce  $\text{HgI}_2$  platelets in horizontal furnaces. The Faile method promises to produce good quality platelets in a short growth period (within days) with the use of organic materials to enhance the properties of the platelets. To date, however, the role of the organic materials during the actual growth process has not been understood. In the mean time, efforts to obtain high-quality crystals without the use of organic materials have also been reported with encouraging results. Goals of the present project include (1) development of a new method to produce multiple  $\text{HgI}_2$  crystals for small radiation spectrometers, (2) characterization of  $\text{HgI}_2$  crystal properties as a function of growth environment, and (3) fabrication and demonstration of room-temperature-operated high-resolution  $\text{HgI}_2$  spectrometers.

## **Phase I: Experimental Arrangements and Installations**

Phase I partially consisted of the specification, ordering, and delivery of equipment and materials required for the success of the project. Included are the acquisition of a de-ionized water system, a vacuum evacuation system, customized growth furnaces, stock  $\text{HgI}_2$  starting material, and various smaller parts and growth accessories. University of Michigan bidding and construction rules caused numerous delays with program progress, hence the acquisition of many materials was realized late in the first year (Phase I) of the program. A six month delay was caused by the following factors; 1) bidding and purchasing agreement delays for the DI water system, 2) delays with the construction and plant department regarding safety concerns over furnace and pumping installation, and 3) delivery delays for the various equipment after the orders were placed. Regardless, meaningful advances have been achieved, as described in later sections. It is expected that within the next two months that all equipment will be upgraded such that Phase II and Phase III of the project can be completed.

The reverse osmosis deionizing (DI) water system was ordered and has been recently installed. The DI system has a 300 gallon storage tank in which the water is constantly circulated through the system loop and filtered, thereby preventing stagnation and microorganism accumulation. The system also has an ultraviolet filter to dispatch any living organisms that may enter the water loop. A series of filters, the smallest being 0.2 microns, cleans the water such that its ultimate resistivity is 18 M $\Omega$ -cm.

Four horizontal furnaces have been designated solely to the project. One furnace is two feet long, three inches in diameter, and has with three separate thermal zones. The other three furnaces are five feet long, four inches in diameter, and also have three separate thermal zones. Being older technology, the original furnaces were not able to accurately maintain the lower temperatures required for HgI<sub>2</sub> purification and growth. The furnace controllers on the small furnace were upgraded to modern digital controllers, which allows for much more reliable thermal profiles at low temperatures (50°C – 200°C). The upgrade has been tremendously successful, and the larger furnaces are now being upgraded as well.

Custom ampoules for HgI<sub>2</sub> material growth have been designed and tested. The most recent growth ampoules are two inches in diameter and have two glass suspension rods at each end, one of which is hollow and open. The ampoules also have an open tubular glass side port that has been necked down. The end port opening is for loading HgI<sub>2</sub> material into the ampoule and the side port is for vacuum evacuating the ampoule.

Custom ampoules for HgI<sub>2</sub> material purification have been designed and are under test. Purification ampoules are one-inch diameter, five-foot long Pyrex tubes with quick connect vacuum outlet on one end. The long ampoules are permanently stationed in the long four-inch diameter furnaces (except during cleaning procedures). Open-ended cylindrical glass boats are used for the purification process (described later).

Under construction is a gas handling manifold and purification system. The system consists of a series of valves and gas filters, and will be capable of treating hydrogen, oxygen, argon, and corrosive gas filters. The system is hooked to a vacuum pump, thus allowing for the HgI<sub>2</sub> growth ampoule to be vacuum evacuated and subsequently filled with a process gas before final closure. A vacuum meter is integrated with the system to accurately determine the vacuum and gas pressure.

## Experimental Procedure and Results

All growth and processing are performed at the Semiconductor Materials and Radiological Technologies (*S.M.A.R.T.*) Laboratory at the University of Michigan. Stock  $\text{HgI}_2$  is loaded by inserting a long-stemmed funnel into a growth ampoule end tube opening and pouring a pre-measured amount of stock material into the ampoule. The long stem ensures that the  $\text{HgI}_2$  is deposited at the bottom of the ampoule. The ampoule end tube is then sealed at the tip and the side evacuation tube is connected to the vacuum evacuation system. After reaching the predetermined vacuum for the growth experiment (and gas environment for future growths), the ampoule is sealed. The ampoule is then suspended within the small three-zone furnace by the glass suspension rods (see Figure 1). All growth runs to the present date have been conducted in a vacuum (no gases). These early runs have been conducted to determine the best parameters for growing reasonably large crystals.

Early experiments have shown that the growth starting conditions are important to the successful growth of relatively large crystals. Early growth runs were conducted by inserting the ampoules into a furnace that was already warmed to the desired thermal profile. The early thermal profiles had the following settings: End Zone 1 (six inches long) =  $200^\circ\text{C}$ , Middle Zone 2 (12 inches long) =  $130^\circ\text{C}$ , End Zone 3 (six inches long) =  $90^\circ\text{C}$ . The ampoule was allowed to rest in the furnace for 5 days, after which it was removed for examination. Figure 2 shows the results from an early growth run. It should be noticed that the  $\text{HgI}_2$  crystals are virtually microscopic, which is interesting for study, but impractical for radiation detector development. It became clear after the results were repeated several times that the growth parameters had to be changed.

The first change made was the thermal profile, which was lowered for many growths with a variety of profiles. For instance, many growths had the following profile: End Zone 1 =  $170^\circ\text{C}$ , Middle Zone 2 =  $115^\circ\text{C}$ , End Zone 3 =  $90^\circ\text{C}$ . Simply lowering the temperature continued to produce results very similar to the crystals shown in Figure 2. Hence, lowering the temperature of the growth did not adequately address the problem.

The initial starting parameters were then changed. The ampoules were loaded into a cold furnace, and the thermal profile was slowly brought up to the growth temperatures of: End Zone 1 =  $160^\circ\text{C}$ , Middle Zone 2 =  $105^\circ\text{C}$ , End Zone 3 =  $90^\circ\text{C}$ . The slowly

warmed ampoule allowed for crystals to nucleate and grow much larger, as shown in Figure 3.

The process was further improved by changing the initial starting material from powder form to solid form, thereby reducing the material sublimation rate and the resulting crystal nucleation and growth rate. Solidification consisted of a two-step process. First, a sealed ampoule was placed in the furnace and the starting  $\text{HgI}_2$  powder material was sublimed and vapor transported from the end to the ampoule center where it condensed. Afterwards, the thermal profile was changed such that the  $\text{HgI}_2$  material was driven back to the end, whereby it condensed as a solid piece. The ampoule was then removed from the furnace and the furnace was allowed to cool down to room temperature. The growth procedure, as previously described, was then implemented, with a reduced lower thermal profile (End Zone 1 =  $135^\circ\text{C}$ , Middle Zone 2 =  $115^\circ\text{C}$ , End Zone 3 =  $90^\circ\text{C}$ ). The resulting crystals, shown in Figure 4, were larger than previous runs. However, it was noticed that many of the large crystals formed in the  $\beta$ -phase, as was indicated by their yellow color when the ampoule was removed from the furnace. The large crystals reformed in the  $\alpha$ -phase as they cooled, causing the crystals to form as polycrystalline.

The technique was repeated for another sample, where the stock  $\text{HgI}_2$  powder was resublimed into a solid mass at the end of the ampoule. The slow warming growth procedure was then implemented, with the thermal profile further reduced to prevent the formation of  $\beta$ -phase crystals in the growth zone (End Zone 1 =  $120^\circ\text{C}$ , Middle Zone 2 =  $100^\circ\text{C}$ , End Zone 3 =  $80^\circ\text{C}$ ). The resulting crystals, shown in Figure 5, were the largest grown thus far, with diameters being larger than 6 mm for many. Crystals of this size (5 mm or more) are large enough to evaluate material properties and make useful X-ray and low energy gamma-ray detectors. Crystal twinning is apparent on some samples, but polycrystalline samples did not form.

It was also noticed that a yellow and orange residue remains at the *source* end of the ampoule. Although the starting material was labeled as high purity (acquired from Alfa-Aesar), the residue is a deposit of impurity material left behind by the vapor transport growth. Hence, the starting material is contaminated with excessive impurities. It will be necessary in the next two years to implement a purification process for the  $\text{HgI}_2$

material before the growth ampoules are loaded and sealed. Condensed matter was found inside of the hollow glass fill handle as well, which is assumed to be the more volatile portions of the stock  $\text{HgI}_2$  material. Purification may also reduce the quantity of the over-volatile material.

### **Improvements for Phase II and Phase II**

During phase II, many major changes are to be investigated. It was observed that a slowly warming ampoule produced the largest crystals. A new growth design will be implemented in the next growth runs, in which glass capillary tubes will be inserted into the furnace beneath the growth ampoule. The glass tubes will have nozzles pointing towards the ampoule, and dry nitrogen will be forced through the capillaries such that they cool pre-appointed spots (or regions) on the ampoule wall. The cooling will provide a zone where the  $\text{HgI}_2$  can selectively grow and will further slow down the temperature increase. It was observed that largest crystals grew in a region of approximately  $115^\circ\text{C}$ , hence the nitrogen-cooled spots will, at first, be adjusted to meet that criteria.

During phase II, the starting  $\text{HgI}_2$  material will be purified in the following fashion. Purification begins with stock  $\text{HgI}_2$  powder material being loaded into a small glass boat and inserted into a 5-foot long narrow glass cylinder. The material is heated such that it sublimates and then condenses at the far end of the cylinder into a receiver boat, thereby leaving behind deleterious impurities (see Figure 6). The receiver boat is inserted into another five-foot purification tube and the process is repeated. Sublimation purification is performed several times and the resulting material is harvested. The harvested material is then sealed into a small glass ampoule. A thorough baking procedure is implemented at a high enough temperature ( $300^\circ\text{C}$ ) to melt the  $\text{HgI}_2$  such that residual impurities are further removed from the material. The resulting material is then removed from the small ampoule. A last step includes multiple zone refinement of the final product, requiring the construction of a small zone refinement furnace. After these steps, the material is ready for crystal growth.

Also during phase II, the initial gas enhanced growth processes will begin. Growth ampoules will be loaded with the purified material as previously described. Afterwards, the ampoule will be backfilled (but still under vacuum) with different gases,

such as argon, oxygen, hydrogen, nitrogen, and a variety of corrosive gases. The differences in growth will be documented. Crystals large enough for evaluation will be harvested and the material properties evaluated, including resistivity, crystallinity, charge carrier mobility, charge carrier mean free drift times, and ultimately radiation detector performance. Radiation detectors will be fabricated from these crystals showing the most promise and tested with gamma-ray sources for energy resolution and durability.

Again, also during phase II, the growth technique will incorporate several growth passes as follows. The growth will proceed as is experimentally determined the best technique. After a few days a growth, however, the thermal profile will be reversed and the growth is continued. This will cause the HgI<sub>2</sub> material, in vapor form, to pass several times over the optimal crystal growth zone, thereby yielding even larger crystals.

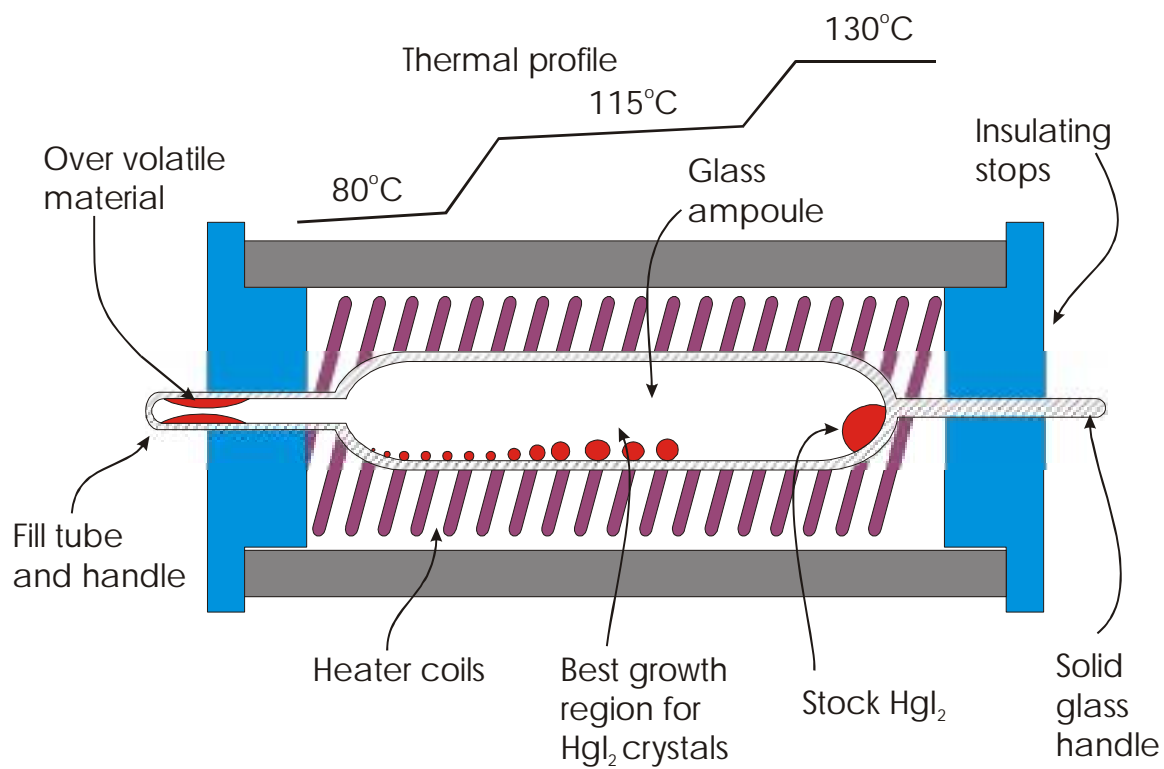
During phase III, the third year, the process will be upgraded to the large four-inch diameter, five-foot long furnaces so as to grow much larger crystals. The best of the techniques studied during Phase I and Phase II will be implemented and modified for the larger furnaces and the resulting crystals studied extensively. The advantages of the horizontal growth technique include (1) scalability to very large diameter furnaces (promising larger crystals) and (2) the realization of multiple crystals per ampoule rather than only one (as typically found with vertical growth techniques).

## **Bibliography**

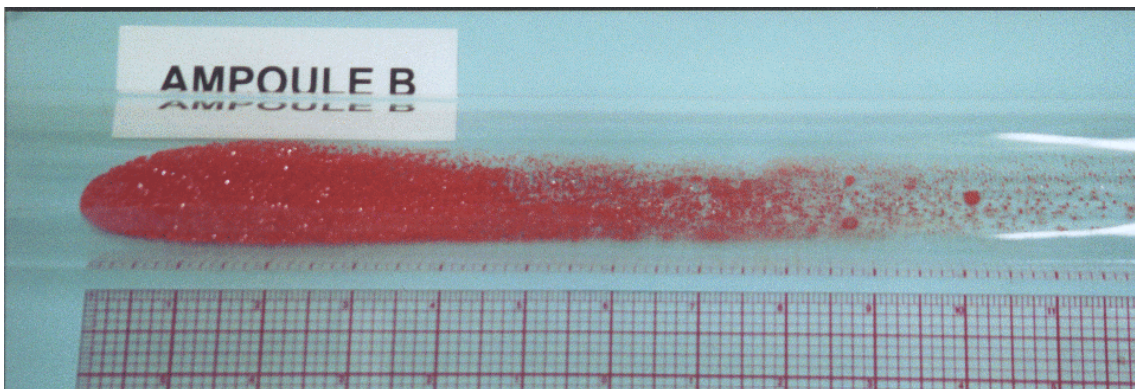
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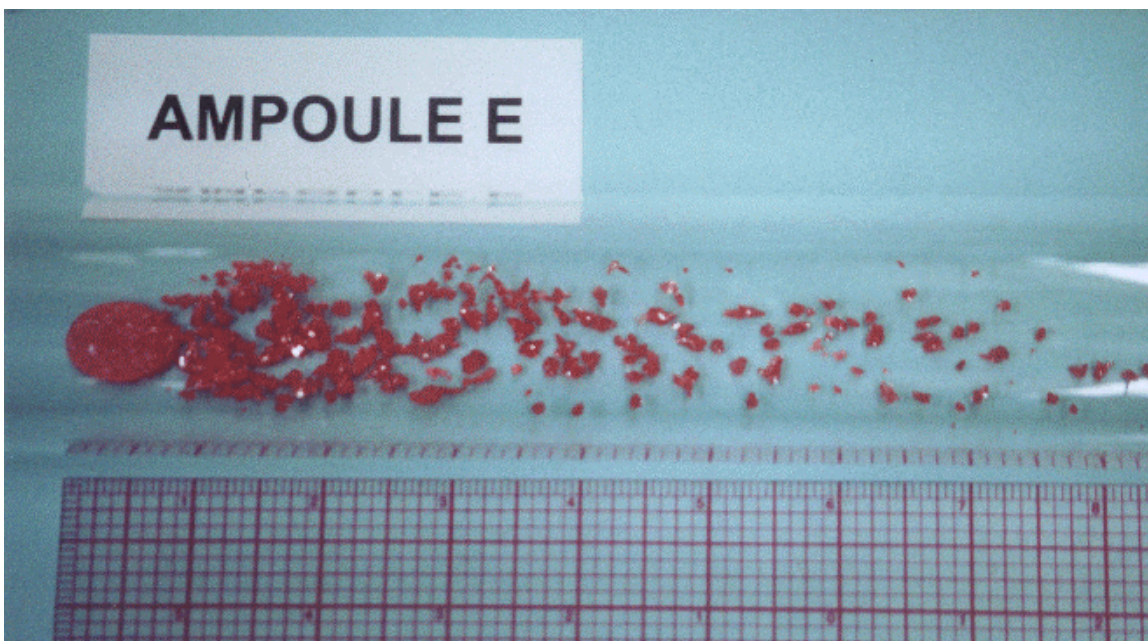
## Figures



**Figure 1: The growth furnace arrangement used in phase I.**

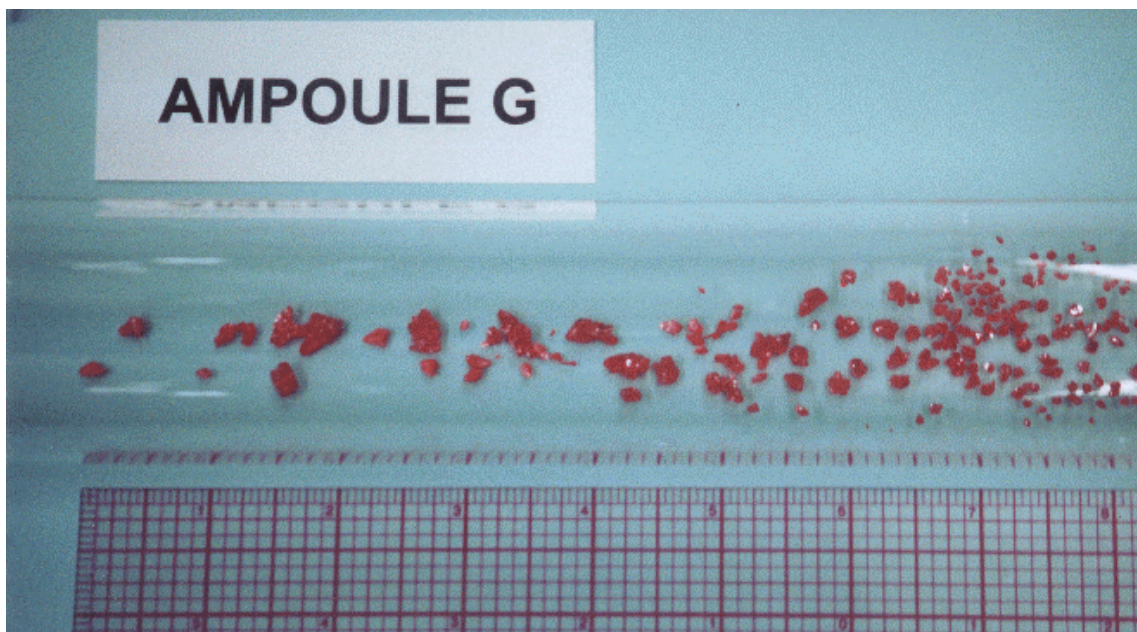


**Figure 2:** Mercuric iodide crystals grown in a preheated furnace, in which the furnace was heated to the growth temperatures before the ampoule was inserted (End Zone 1 = 200°C, Middle Zone 2 = 130°C, End Zone 3 = 90°C). The crystals shown are small in size and impractical for gamma-ray detector use.

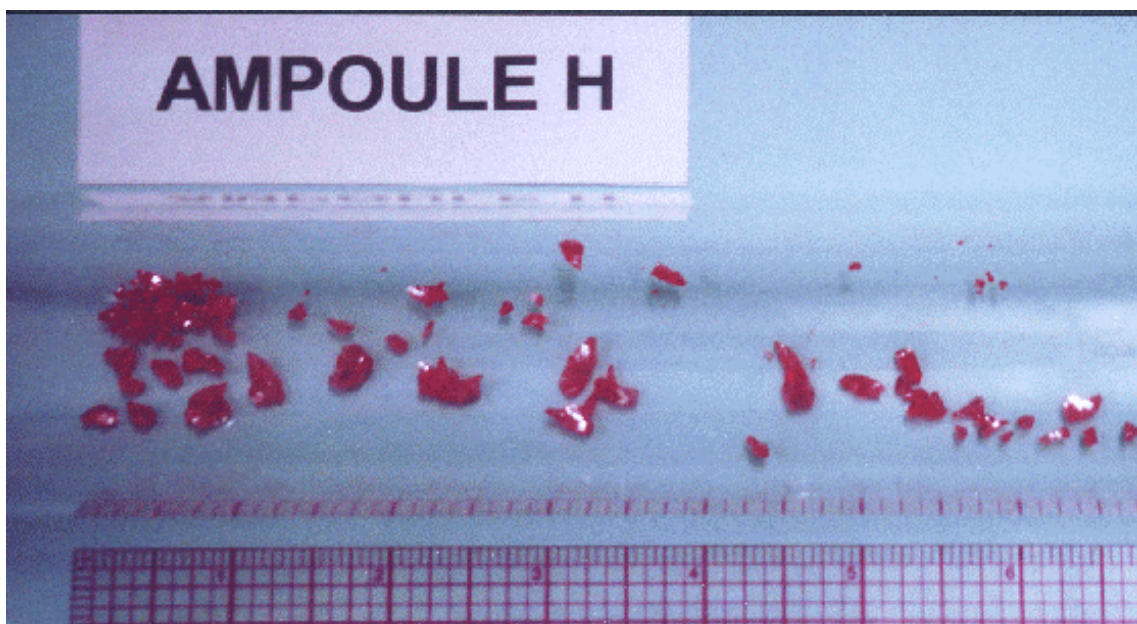


**Figure 3:** Mercuric iodide crystals grown with slow thermal warming and lowered furnace temperatures. The furnace was heated to the growth temperatures after the ampoule was inserted (End Zone 1 = 160°C, Middle Zone 2 = 105°C, End Zone 3 = 90°C). The crystals shown are larger than the crystals grown with preheated furnace conditions.

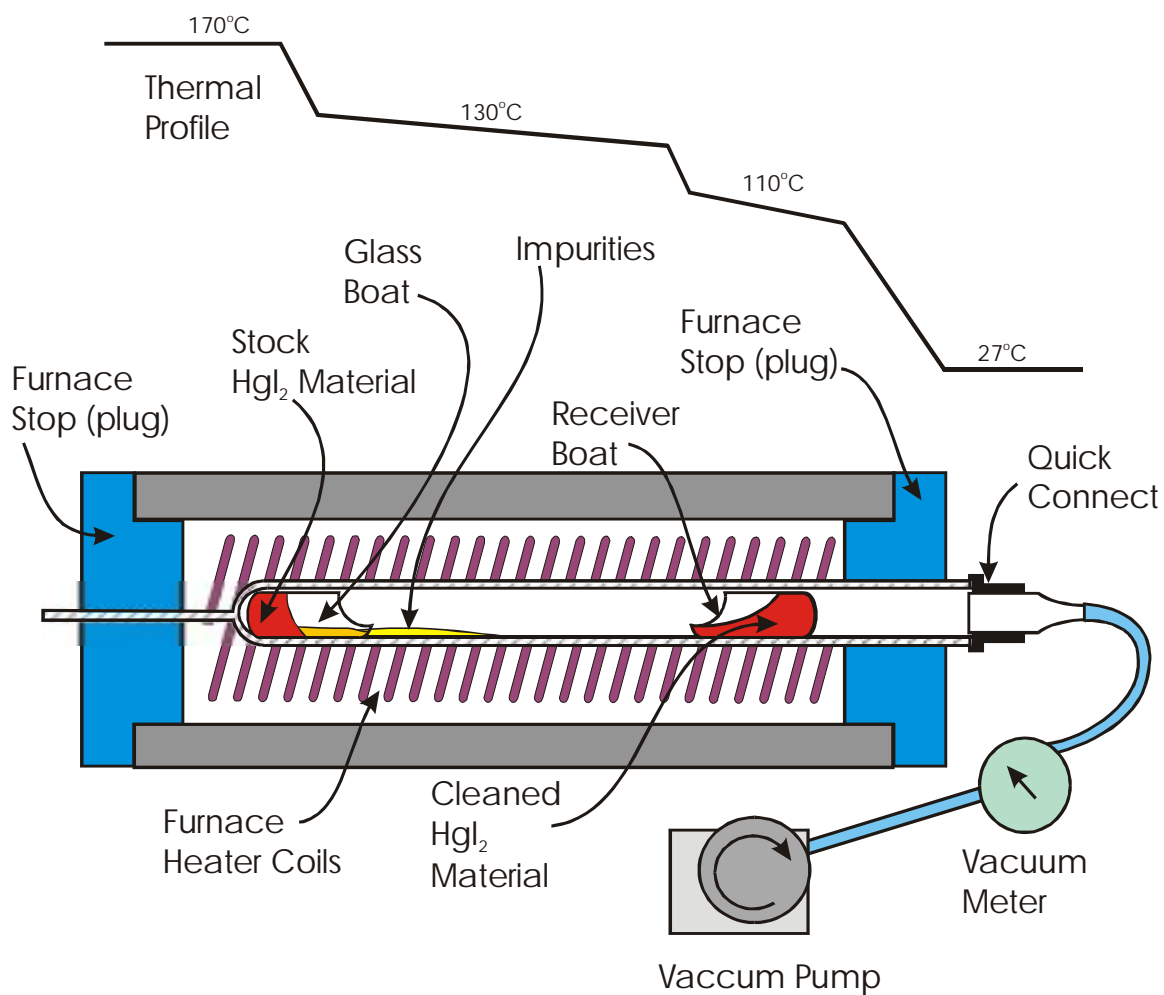




**Figure 4:** Mercuric iodide crystals grown with slow thermal warming at even lower temperatures (End Zone 1 = 135°C, Middle Zone 2 = 115°C, End Zone 3 = 90°C). The crystals showed markedly larger sizes than previous runs, indicating that lower temperatures are better. The crystals show obvious signs of twinning and polycrystalline regions most likely due to  $\beta$ -phase formation in the growth zone.



**Figure 5:** Mercuric iodide crystals grown from a solid source and with slow thermal warming. The temperatures were reduced to prevent the formation of  $\beta$ -phase crystals in the growth zone (End Zone 1 = 120°C, Middle Zone 2 = 100°C, End Zone 3 = 80°C). The crystals again showed markedly larger sizes than previous runs, and the crystallinity appears much better, showing much fewer twinned regions. Such crystals have large enough regions that can be used for small gamma ray spectrometers.



**Figure 6: The purification furnace arrangement to be used in phase II.**